# CATALYTIC CONVERSION OF RBD PALM OIL TO FUEL : THE EFFECT OF SILICA-ALUMINA RATIO IN ZSM-5

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## ABSTRACT

The refined, bleached and deodorized (RBD) palm oil was converted to Organic Liquid Products (OLP) by passing it's the vapor through ZSM-5 catalyst. The constituents of OLP consist of gasoline, C12-C15, and other type of organic liquid. The equipment that was used to carry out the experiment was modified based on the suitability of the substance used. There are three types of ZSM-5 that were used to investigate the effect of ratio of silica oxide to the alumina oxide (23 SiO2/Al2O3). From recent research has showed that zeolite ZSM-5 with the ratio of 23 SiO2/Al2O3 will produce the highest OLP amount in which are about 96.9%. The alumina oxide in ZSM-5 is the one that influences the strength of the acid site zeolite. Therefore, the relationship between the two is inversely proportional, which when the ratio is lower, the higher the strength of the acid will be. The ratio of 23 SiO3/Al2O3 is the smallest ratio when compared to the other three catalysts than were used. The rate of conversion of palm oil to OLP is influenced by the concentration of acid site. All the OLP was analyzed with Fourier Transform Infrared (FTIR) in order to detect the functional group of alkanes, alkenes and aromatic. The products was analyzed and shown that the functional groups is presence, which showed that all the ratio that was used can convert palm oil to OLP.

# ABSTRAK

Minyak kelapa sawit (RBD) ditukarkan kepada Cecair Organik (OLP) dengan melalukan wapnye melalui mangkin ZSM-5. Kandungan OLP adalah terdiri daripada gasoline, $C_{12}$-$C_{15}$ dan lain-lain cecair organic. Radas yang digunakan telah diubahsuai mengikut kesesuaian bahan yang digunakan. Tiga jenis ZSM-5 digunakan untuk mengkaji pengaruh nisbah silika oksida terhadap alumina oksida (23 $SiO_2/Al_2O_3$) . Hasil daripada kajian menunjukkan bahawa zeolite ZSM-5 yang bernisbah 23 $SiO_2/Al_2O_3$ akan menghasilkan OLP yang paling banyak iaitu 96.9%. Kandungan alumina oksida dalam ZSM-5 akan mempengaruhi kekuatan acid site zeolite tersebut. Oleh sebab itu, semakin rendah nisbah $SiO_2/Al_2O_3$ maka semakin tinggi asid di dalam zeolite ZSM-5. Nisbah 23 $SiO_2/Al_2O_3$ adalah nisbah yang terkecil di antara ketiga-tiga jenis mangkin yang telah digunakan. Ini menunjukkan kadar penukaran minyak kelapa sawit kepada OLP dipengaruhi oleh asid secara langsung. Ketiga-tiga OLP yang diperolehi telah dianalisa dengan FTIR bagi mengesan kehadiran kumpulan berfungsi iaitu alkana, alkene dan aromatic. Ketiga-tiga hasil ujikaji yang dianalisa menunjukkan kehadiran kumpulan berfungsi tersebut, ini boleh disimpulkan zeolite yang digunakan mampu menghasilkan OLP daripada minyak kelapa sawit.

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## LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| LPG | - | Liquid Petroleum Gas |
| LNG | - | Liquid Natural Gas |
| CNG | - | Compressed Natural Gas |
| RBD | - | Refined, Bleached and Deodorized |
| $SiO_2/Al_2O_3$ | - | Silica Alumina |
| $CO_2$ | - | Carbon Dioxide |
| FTIR | - | Fourier transform Infra Red |
| WHSV | - | Weight Hour Space Velocity |
| OOP | - | Other Organic Products |
| OLP | - | Organic Liquid Products |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

In this new era, people around the world is chasing for development, luxury, own benefits and interest without thinking about others. Many hard situation faced by government around the world caused by global problems. As such problem is the increase of global fuel price, which causes for community to seek new methods that are low cost and high efficiency in producing fuel. The main reason for the push for new method of fuel production is due to the depleting petroleum or natural gas resources. The amount of petroleum reserves now is not enough to support today's demand and the future because of many challenges and obstacle faced by the producer countries. Many factor affect the production of petroleum around the world, as such factors are war, natural disaster, political and speculation factor. Hence, many discoveries are made in finding alternative to problems faced such as production of fuel from palm oil. The oil is extracted from the palm seed that can be converted to Organic Liquid products (OLP) by reaction with catalysts ZSM-5 under specific alumina-silica ratio. The components of OLP are gasoline, $C_{12}$-$C_{15}$ and Other Organic Products (OOP).

The main advantages of using this alternative fuel are its renewability, better quality of exhaust gas emissions, its biodegradability and given that all organic carbon present is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect. One of the disadvantages of using this alternative is the higher cost of production result from the high price of raw material compare to fossil fuel.

The fast depletion of fossil fuels coupled with the increasing awareness of environmental issue, concern for increasing green house gas emissions and escalating petroleum price, have led Malaysia to concerted efforts in the search for renewable and environmentally friendly alternative energy source. The Malaysian government is refocusing the use of palm oil to cater to the huge demand from European countries, it has encouraged the building of biofuel plants. Palm oil is a form of edible vegetable oil obtained from the extraction of the palm fruit. Over the past two decades, Malaysia's total oil palm planted area increased from 640 000 hectares in 1975 to 4.17 million hectares in 2006. The total oil palm planted area driven mainly in Sabah and Sarawak with a combined of 4.5% versus Peninsular Malaysia's 1.6%.

**1.2 Palm Oil**

The Malaysian palm oil industry has grown rapidly over the years to become the world's largest producer and exporter of palm oil and it products. In 2003 more than 3.79 million hectares of land were under oil palm cultivation, occupying more than one-third of the total cultivated area in Malaysia and 11% of the total land area. In the same year production of palm oil in Malaysia had reached 13.35 million tonnes of crude palm oil and 1.64 million tonnes of crude palm kernel oil which was an increase of app. 12% over that of the previous year.

Malaysia's production of palm oil in 2003 contributed to about 49 percent of world palm oil output and 8.9% of world output of the 17 major oils and fats. The world demand for palm oil is expected to increase with respect to the competitive

prices and energy efficient production of palm oil along with the growing markets globally especially in big country like China and India.

Being involved in three sectors, namely agriculture, transport and industry the production of palm oil faces a triple environmental challenge which must be monitored and dealt with. With a vast use of fertilizer in the plantations, poorly maintained transportation trucks exhausting black clouds as the go and emissions from the mill, the industry has both environmental responsibilities to live up to and money to save by making the right technological investments and incorporating environmental management.

During the last few years, environmental issues are increasingly becoming more important in Malaysia and the world over. The palm oil industry is aware of the environmental pollution and is striving towards quality and environmental conservation through 'sustainable development and cleaner technology approach. Thus, to remain competitive the oil palm industry must be prepared for new challenges ahead. Self regulated environmental management tools like the ISO 14000, EMAS and Life cycle assessment could be adopted by the palm oil industries to structure their environmental efforts to the benefits of themselves and the environment.

## 1.3 Gasoline

Gasoline was not being invented but it is a natural by-product of the petroleum industry and kerosene being the principal product. Gasoline is produced by distillation, the separating of the volatile, more valuable fractions of crude petroleum. However, what was invented were the numerous processes and agents needed to improve the quality of gasoline making it a better commodity.

Gasoline is one of the petroleum-based fuels that have an essential function in the industrial economy of a developing country and used for transport of industrial and agricultural goods and operation of gasoline tractor and pump sets in agricultural sector. The price of gasoline is soaring in these last years and it will be exhausted some day. A lot of efforts have been carried out to develop on alternative fuel for the current energy and transportation vehicle system such as methanol, ethanol, compressed natural gas (CNG), liquefied petroleum gas (LPG), liquefied natural gas (LNG), vegetable oils, reformulated diesel and reformulated gasoline fuel have all been considered as alternative fuels.

Gasoline is a mixture of fuel that has been produced from petroleum consisting mostly of aliphatic hydrocarbons, enhanced with iso-octane or the aromatic hydrocarbons toluene and benzene to increase its octane rating and is primarily used as fuel in internal combustion engines. . The mixture of hydrocarbons, although some may contain significant quantities of ethanol and some may contain small quantities of additives such as methyl tert-butyl ether as anti-knock agents to increase the octane rating. The hydrocarbons consist of a mixture of n-paraffins, naphthenes, olefins and aromatics. Naphthenes, olefins and aromatics increase the octane rating of the gasoline whereas the n-paraffins have the opposite effect.

### 1.3.1 Cracking

There was a need for improvement in the refining process for fuels that would prevent engine knocking and increase engine efficiency. Especially for the new high compression automobile engines that were being designed. The processes that were invented to improve the yield of gasoline from crude oil were known as cracking. In petroleum refining, cracking is a process by which heavy hydrocarbon molecules are broken up into lighter molecules by means of heat, pressure, and sometimes catalysts.

### 1.3.2 Catalytic Cracking

Eventually, catalytic cracking replaced thermal cracking in gasoline production. Catalytic cracking is the application of catalysts that create chemical reactions, producing more gasoline. The catalytic cracking process was invented by Eugene Houdry in 1937.

### 1.3.3 Others Processes

Other methods used to improve the quality of gasoline and increase its supply including:

- Polymerization - converting gaseous olefins, such as propyl butylene, into larger molecules in the gasoline range.
- Alkylation - a process combining an olefin and a paraffin such as isobutene.
- Isomerization - the conversion of straight-chain hydrocarbons to branched-chain hydrocarbons.
- Reforming - using either heat or a catalyst to rearrange a molecular structure.

## 1.4 Crude Oil

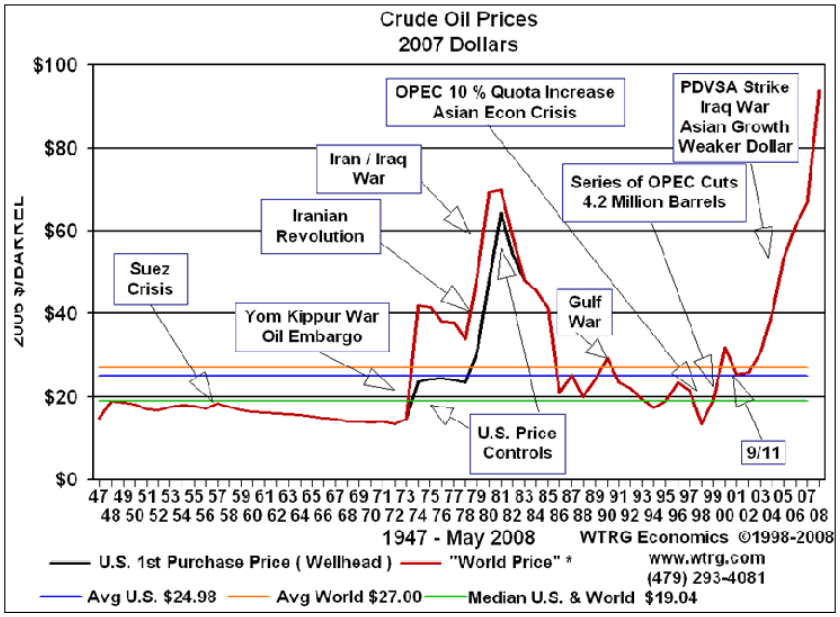


**Figure 1.1: Crude Oil Prices 1947**

Oil companies won't be building more refineries, because there won't be enough oil left to refine by the time new refineries could pay for themselves. There hasn't been a new refinery built in the US since 1976. In 1982, there were 301 operable refineries in the U.S and they produced about 17.9 million barrels of oil per day. Today there are only 149 refineries, and they're producing 17.4 million barrels. This increase in efficiency is impressive but not a miracle. As with everything these outputs are carefully calculated to optimize profitability.

The world at large consumes 30 billion barrels of oil per year, and the top oil consumers largely consist of developed nations. In fact, 24% of the oil consumed in 2004 went to the United States alone. The production, distribution, refining, and retailing of petroleum taken as a whole represent the single largest industry in terms of dollar value on earth.

## 1.5 Problem Statement

Nowadays, fuel is most valuable source in the world because this source are become decrease follow the year. It is because, fuel is a very important sources to generate the energy that widely used in commercial, industrial and transportation. Natural gas one of the alternative to produce gasoline, but the problem of transportation and safe handling of the gas makes it difficult to distribute the gas to rural areas. Coal investment in liquid fuel production had almost ceased after exploration of the petroleum around a half-century ago.

Bio-fuel appears as a promising alternative for petroleum. The reasons of using bio-fuel because it comes from renewable sources, is environmental friendly due to low sulfur and nitrogen content, do not contain any toxin or poison, full of energy, easy on handling and transportation, as it appears in liquid form and can be operate at winter time that has a temperature of -20$^{o}$C and above.

As viscosity of palm oil is very high, a suitable method to crack the triglycerides is essential. Low in selectivity of organic liquid products is the main problem in this research and it seems that it is not commercially viable. The research palm oil catalytic cracking has a bright prospect in the future. More studied have to be done to make sure this process is economically viable. The ultimate challenge still lies in catalyst development. A stable, shape selective and high acidic catalyst is needed in order to achieve high conversion and selectivity in this process.

The researchers in this field also agree that the process of converting palm oil to OLP depend on the acidity of the catalysts, especially Bronsted acid. Therefore, this research will try to find the suitable for the catalytic cracking of palm oil to organic liquid products (OLP). ZSM-5 catalyst follow specific silica-alumina ratio in order to achieve higher percentage of organic liquid production. ZSM-5 is chosen as catalyst in this process because it has better characteristic and properties than other type of catalyst.

## 1.6 Objective

The objective of this study is to determine the catalytic conversion of refined, bleached and deodorized (RBD) palm oil to organic liquid products (OLP) by using silica-alumina ratio in ZSM-5 as catalyst with help of fixed-batch reactor.

## 1.7 Scope of Research Works

i) To study the effect of ratio silica-alumina in catalyst HZSM-5 in producing organic liquid products (OLP) from palm oil.
ii) To study the selectivity OLP that produced by catalytic conversion of palm oil.

## 1.8 Rational Significant

Nowadays the price fuel is rapidly increased due to limited source because this fossil fuel is non-renewable energy. Therefore, strong needs to find the alternative fuel source of petroleum. This research is about to find the alternative fuel to replace fossil fuel as primary source of energy. The palm oil had been study the potential to produce alternative fuel because the raw material is abundant. Besides that, this fuel has many advantages such as environmental friendly due to low sulfur and nitrogen content and easy on handling and transportation, as it appears in liquid form.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

The majority of the world's energy is supplied by petroleum derived fuels and petroleum based distillates are used in a wide range of industrial applications. Petrochemicals serve as raw materials for the chemical industry in the production of solvents, lubricants, paints, and lacquers. The spectacular growth in consumption of crude petroleum during the middle and late twentieth century can be attributed to the ease with which petroleum can be discovered, produced, transported, processed, and utilized. The oil crisis in the 1970s, depleting reserves, national scarcity issues, price uncertainty, and growing environmental concern over the combustion of fossil fuels highlight major issues associated with the extensive use of petroleum in our society.

Since the rise of gasoline in the world market, a lot of efforts have been carried out to develop an alternative fuel for the current energy and transportation vehicle system, i.e.: fuel cell, electric power, hydrogen, biodiesel , bioalcohol, vegetable oil, natural gas for internal combustion engines and other biomass source.

The alternative gasoline fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. There are some advantages that justify biofuel development. It not only provides a market for excess production of vegetable oils but also can decreases although will not eliminate, the

country's dependence on imported petroleum. Biofuel is renewable and does not contribute to global warning due to its closed carbon cycle. A life cycle analysis of biofuel showed that overall carbon oxide emissions were reduced by 78% compared with petroleum-based gasoline fuel. This fuel is biodegradable and non-toxic. This alternative also given that all organic carbon present in photosynthetic in origin. So, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere if all of the energy input for the biofuel production are non-fossil based and consequently to the green house effect.

Vegetable oils are attracting increased interest in this respect. Many researchers improved the production of hydrocarbons and chemicals from plant oils using catalytic cracking processes. The vegetable oils that have been investigated as alternative fuels are canola oil, tall oil, and jajoba oil. These plant oils were converted to hydrocarbon over many types of catalysts such as ZSM-5, hydrogen-zeolite Y, silica-alumina, H-mordenite, and silica-alumina pillared clay at a temperature range of 300 – 500 °C. Over 95 wt% of the plant oils were converted to liquid hydrocarbons in the gasoline boiling range, light gases, and water.

Palm oil has been converted into a more compatible form of methyl ester known as biodiesel, by the Palm Oil Research Institute Malaysia (PORIM). The biodiesel was developed to substitute the diesel for engines. Rapeseed, sunflower, and soybean oils are examples of oils used in methyl ester production. There is a need for a direct conversion process for converting palm oil to clean premium transportation fuels and chemicals.

The shape selective zeolite catalysts have been used for catalytic cracking and the medium pore size catalyst such as ZSM-5 was found to be more efficient in the cracking process and in the organic liquid production. Prasad and co-workers reported that ZSM-5catalyst gave mainly aromatic hydrocarbons. The properties of shape selective catalysts control the product distribution in the process, and therefore, the choice of the shape selective zeolite catalyst is an important factor. Activity and selectivity of these catalysts are governed by several factors, such as acidity, pore size and its distribution, and also the shape of the pores.

Hybrid catalysts were used to improve the shape selectivity of the catalyst. Co-worker reported cracking of canola oil over hybrid catalysts using the mixture of ZSM-5 with silica-alumina and H-Y with silica-alumina. The addition of zeolite catalysts to silica-alumina increased the cracking of canola oil and aromatic hydrocarbon contents. Acidity of a catalyst was determined to be one of the important factors in the cracking process. The conversion was found to decrease with a decrease in catalyst acidity. The acidity of the catalyst influences selectivity of the catalyst. Co-workers reported that potassium impregnation of ZSM-5 catalysts affects the aromatization and oligomerization reactions.

## 2.2 Palm Oil

Palm oil is a form of edible vegetable oil obtained from the fruit of the oil palm tree. It is an important component of washing powders and personal care products. It is also used to treat wounds and has been controversially discovered as a feedstock for biofuel. The other usages of palm oil include cooking oil, margarine and a component of many processed foods. The palm oil source is the palm oil extracted from palm fruit and the fruit seeds. Palm oil is one of the few vegetable oils relatively high in and thus semi-solid at room temperature and can be fractionated into solid and liquid fractions. The solid product is known as stearins while the liquid products are known as oleins. The crude palm oil is can also be processed to yield RBD (refined, bleached, and deodorized) and NBD (neutral, bleached, and deodorized) palm oil, which are used in daily activities. The process can be done through physical or chemical refining treatment respectively. Figure 2.1 shows the three processes that can be done with crude palm oil. Fractionation process is employed to crude palm oil to produce crude stearin in solid form and crude olien in liquid form. The crude olein and stearin then will undergo either physical or chemical refining process to produce refined, bleached, and deodorized (RBD) stearin and olien.

Crude palm oil is also can be directly processed via physical refining. In this type of refining, crude palm oil is separates to palm fatty acids distillates and RBD palm oil. In chemical refining process, crude palm oil is separated to palm acid oil and neutral, bleached, and deodorized (NBD) palm oil. Fractionation process is employed to both RBD palm oil from physical refining and NBD palm oil from chemical refining to obtain RBD stearin and olien.